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A CHLORITE HOLOPULPING METHOD TO EVALUATE STRENGTH CHANGES IN TMP

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ABSTRACT

A chlorite holopulping method was used to evaluate the wood chips and fiber from the primary refiners, secondary refiners, and latency chest of Bowater's Calhoun, Tennessee TMP Mill. Testing was carried out during the winter, spring, and summer to evaluate the source of seasonal strength changes observed by the mill. The results show that the seasonal strength changes can be traced to changes in the native fiber strength of the wood chips. The fiber weakness shows up as low wood chip and refiner holopulp zero-span tensile index and low holopulp tear index at constant tensile index for the winter samples. Fiber length is also lower in the winter samples. An analysis of the wood chips for the three seasons evaluated shows a slight increase in oversized chip content and decrease in average wood chip density during the winter. In addition, there is an increase in the number of large growth ring wood chips in winter samples. This is indicative of a higher juvenile wood or plantation wood content. The change in wood density observed is sufficient to induce the changes in strength observed in the mill and is related to the juvenile wood/plantation wood content of the chip supply.

INTRODUCTION

Papers made from mechanical pulps are generally fiber bonding limited structures.[1] In an ideal bond limited paper, fibers pull out of the sheet at failure and relatively few fibers break. Tensile and tear strength depend only on surface area and bond shear strength. However, for sulfite chemithermomechanical pulp[2] (CTMP), alkaline peroxide chemimechanical pulps[3] (APMP), and low freeness thermomechanical pulps (TMP),[4] tear index goes through a maximum with increasing specific energy and begins to decline with additional refining. These pulps reach the point where bond strength exceeds fiber strength and the paper will benefit from improved processing to preserve the native strength of the wood fibers. To avoid fiber strength losses in high yield pulping, it is important to consider fiber damage that occurs early in the process. Fiber damage in chipping, chip handling, chip compression in the plug screw feeders, and the initial size reduction in the first stage refiner, may increase the susceptibility of the fiber to cleavage later in the process.

The conventional method of evaluating damage that occurs early in the refining process is to complete the refining under controlled conditions and pass judgement on the merit of the chip treatments and early stage refining by the effects observed on final pulp quality. Overall, this is not a bad concept, final pulp quality is the issue of real commercial interest. Unfortunately, the concept of control in refining is as much a goal as a reality, and the remaining uncontrolled process instability limits the sensitivity for detecting change.

Ideally, to understand the process, it is vital to separate paper strength into its component parts - fiber strength, surface area, relative bonded area, and specific bond strength - and to be able to evaluate the progress in developing each of these components throughout the chip treatment and refining process. This project has evaluated a chemical delignification method for measuring fiber strength throughout the refining process and applied it towards understanding the seasonal TMP strength variation at the Bowater mill in Calhoun, Tennessee.

A room-temperature, acetate-buffered chlorite technique was selected as the delignification method for the project. Chlorite holopulping provides a means to selectively delignify wood at any point in the wood handling and pulping process.[5,6] Handsheet testing has the advantage of using a fully representative sample of the wood or pulp. Although fiber bond strength, fiber strength, and the presence of handsheet defects all influence handsheet strength, these problem can be minimized by relying on zero span[7] tensile testing and both the tensile and tear indices[8,9] as a measure of fiber strength. Handsheet defects, such as shives and variations in basis weight, will increase the standard deviation in the handsheet testing. These can be controlled by proper preparation of the pulp for sheet forming. Delignified pulps were evaluated for Kajaani fiber length and handsheet testing of zero-span tensile index, tensile index, and tear index.

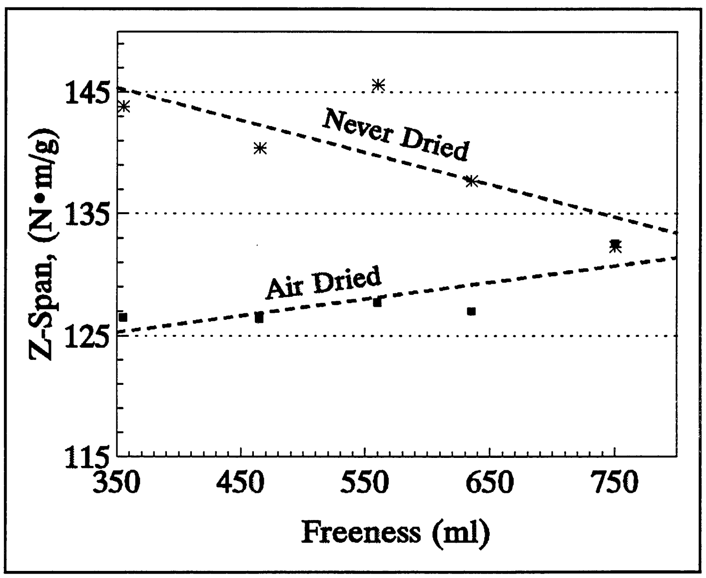

Figure 1. Zero-Span Tensile Index for the beater run samples.

INFLUENCE OF HOLOPULPING ON HANDSHEET STRENGTH

A series of tests was carried out on a sample of wood chips. The chips were chlorite delignified and the resulting pulps beaten in a PFI mill to 0, 2300, 4000, 6500, and 9000 revolutions, giving freeness levels ranging from 760 to 355. Half the sample at each freeness level was air dried. TAPPI handsheets were then made from each sample giving sets for 5 freeness levels and air dried vs. never dried. Handsheets were tested for zero-span tensile, tensile, tear, burst and optical properties. Pulps were tested for Canadian Standard Freeness (before drying) and Kajaani fiber length.

Results of Beater Testing

The influence of air drying and freeness on pulp zero span tensile is shown in Fig. 1. Although both the air dried and never dried samples appear to give straight line relationships, the slopes are significantly different. Zero-span tensile index decreases about 12 N·m/g (9%) with air drying. With chemical pulps, zero-span tensile strength usually increases with beating, rising to a maximum or broad plateau around 600 ml CSF.[10] In the freeness range of these experiments, the zero span tensile should be nearly independent of freeness. In a multiple regression analysis of the zero-span data, the air drying process and the number of chlorite stages were significant, but pulp freeness was not significant at the 95% confidence level.

The air drying process reduces the tensile index by about 20 N·m/g (25%) at all freeness levels and increases the tear index by about 0.45 mN·m^2/g (5%). The relationship of tear index to tensile index is generally considered to be a better measure of pulp strength than the individual measurements. This data is shown in Fig. 2. The air drying procedure has clearly reduced the tensile index without a corresponding increase in tear.

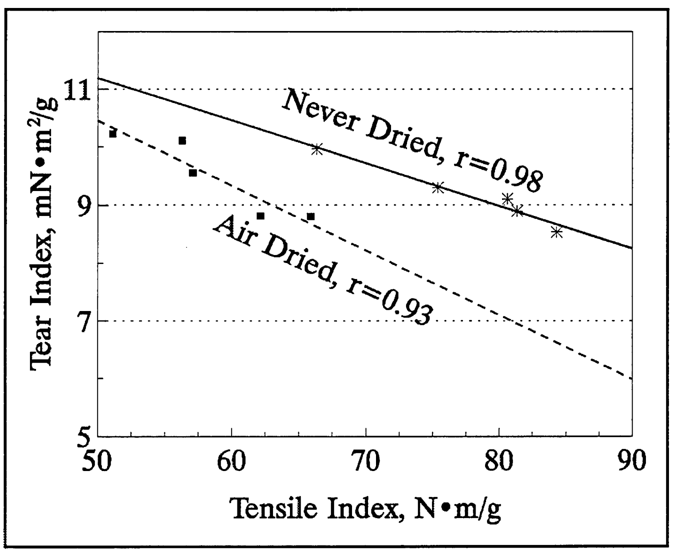

Figure 2. Tear Index plotted against Tensile Index for the control data.

Seasonal Strength at Bowater Calhoun

For each season, the mill supplied samples of wood chips from the chip washer, and fiber from the discharge of the primary refiner, the discharge of the secondary refiner, and the latency chest. Samples were collected twice during the sample period. One set of samples was taken under conditions as closely controlled as possible. The second set of samples was representative of the normal mill operation at the time. Wood chip samples were screened on a Williams Classifier to determine if there was a significant change in chip size distribution between the seasons. All samples were holopulped and analyzed in duplicate.

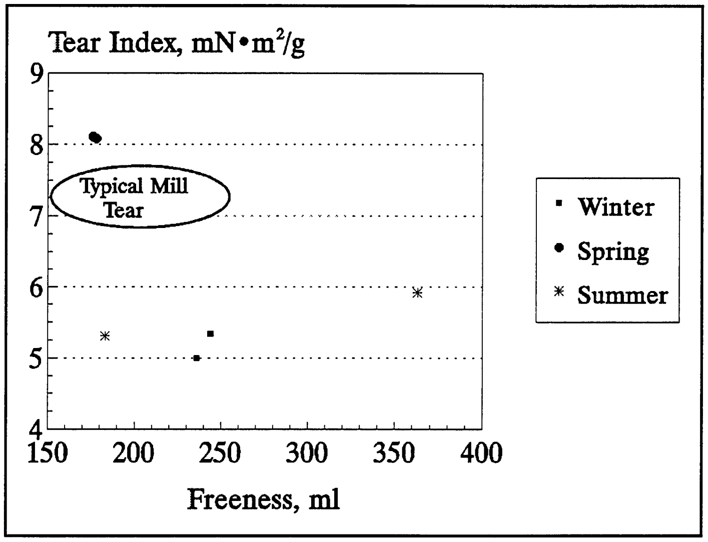

Figure 3. Tear Index plotted against freeness for the latency chest samples (mill data). The region identified as typical mill tear index is from the fall of 1994.

Results and Discussion

The tear index of the latency chest pulp samples is plotted against freeness in Fig. 3. The typical mill tear index averages 7.2 mN·m^2/g with a freeness range from 120 to 230 ml, and appears to be insensitive to freeness in this range. The two samples from the winter collection period confirm the low strengths reported by the mill. The low freeness sample from the summer collection period also shows a low tear strength.

Since freeness was not a significant variable for the zero span tensile testing of the chlorite pulps, the holopulp zero-span tensile data from the three seasonal test periods was pooled and tested for significant differences. The average zero-span data and results of the *t* tests are summarized in Table 1. There are no significant differences between the control and normal production samples from each period, but the spring zero-span tensile strengths are significantly greater than the winter 92/93 and the summer samples. The summer controlled-production zero-span is significantly greater than the winter samples at a 90% confidence level (one tailed t-test). Since the Winter samples were not dried before making the handsheets, these zero-span tensile indexes should be about 12 N·m/g higher than would have been obtained with air-dried samples. This would make both sets of summer samples significantly stronger than the Winter 92/93 samples. The range of zero span tensiles for the

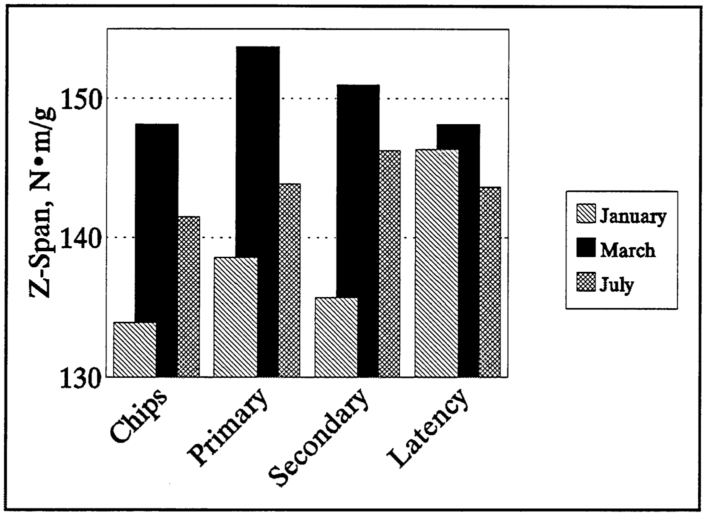

Figure 4. The zero-span tensile data for the normal mill pulps from the three sample periods.

four samples in each set was less than 8% (Fig. 4), confirming the relative insensitivity of the test to beating, and largely justifying the pooling of this data.

The tear/tensile data for the three sample periods and four sample locations are graphed in Fig. 5 as a bar chart showing the sample tear index as a percent of the interpolated control (PFI data) tear index at the sample tensile index. For this graph, the tear index and tensile index data of the standard production and control samples were averaged. The spring samples give the highest relative tear index at all four sample locations. For the wood chips, primary refiner discharge, and secondary refiner discharge, the winter samples have a higher tear index than the summer samples. At the latency chest, the relative tear index of the summer samples exceeds the tear index of the winter samples. The average tear index relative to the controls is shown in the last cluster of bars. The spring samples show the highest overall average test followed by the winter and summer samples in that order.

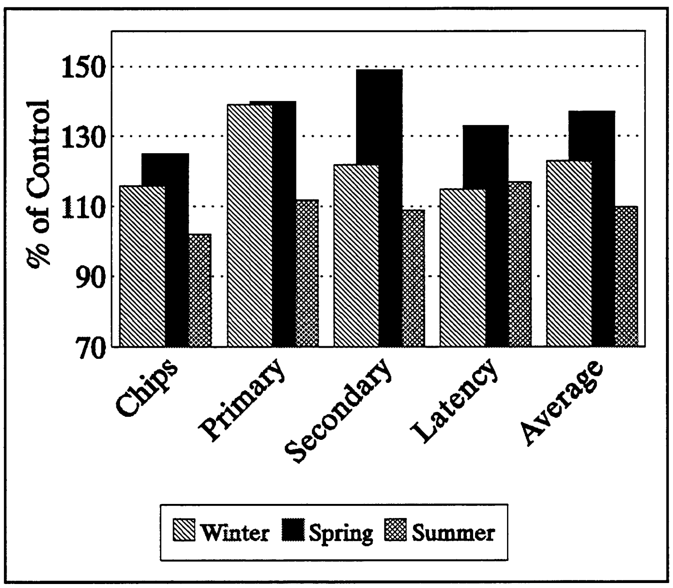

Figure 5. Sample tear index divided by the estimated control tear index at the sample tensile index, expressed as a percentage.

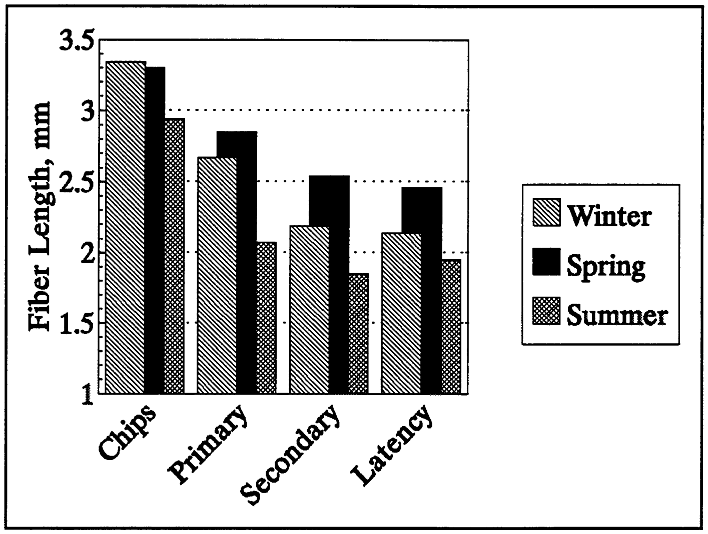

Figure 6. The chlorite holopulp fiber lengths for the controlled refining conditions.

The fiber length for the three sample periods is shown in Fig. 6. Fiber length gives a clear indication of fiber damage in the refiners. The winter and spring wood chips have slightly longer average fiber length than the summer samples. The fiber length decreases substantially between the wood chips and primary refiners in both the winter and summer samples, confirming the fiber shortening expected in high-yield refining. Net fiber length retention from the wood chips to the secondary refiner is 77% in spring, 65% in winter, and 63% in summer for the controlled production samples. The standard production samples had similar losses in fiber length in winter and spring, but the summer sample retained only 48% of the native wood fiber length through the refiners.

Wood Chip Analysis

The chip size distribution changed only slightly during the sample period, with the spring period having the largest retained 13-mm and 6-mm fractions (Fig. 7). There did not appear to be a significant change in the pass 6-mm fraction, but there were considerably more chips retained on the 25-mm screen for both winter and summer samples. The mill TMP pulp test data shows a seasonal loss in both tensile index and tear index for the low strength periods. In contrast, carefully controlled studies of chip size confirm the loss in tensile strength but show relatively little change in tear index when increasing the larger chip content.[11,12] This inconsistency suggests that chip size may not be the source of the reduced pulp strength and may instead be caused by the changes in the wood supply responsible for the

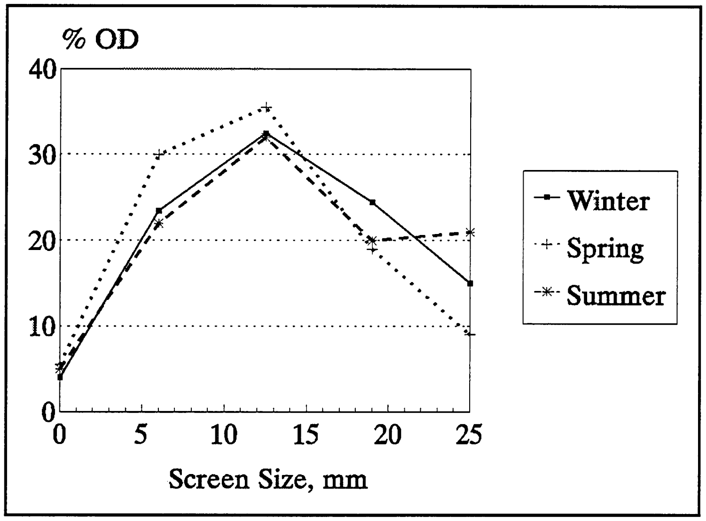

Figure 7. Chip size distribution for the Winter, Spring and Summer samples.

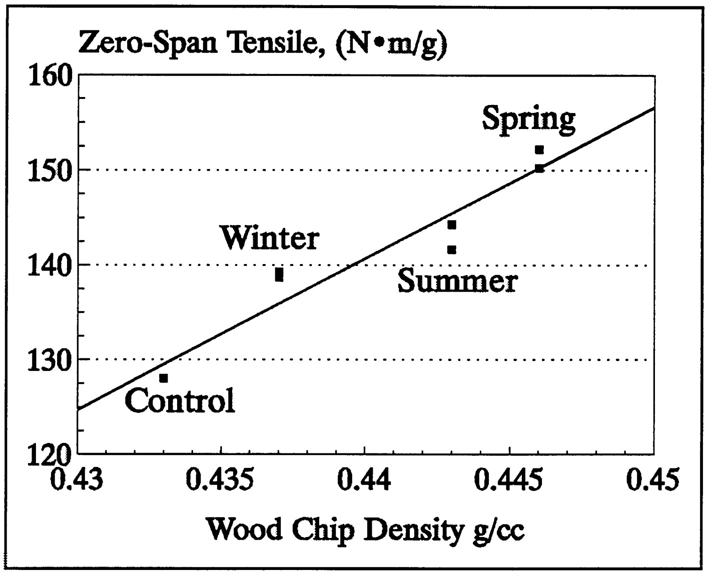

Figure 8. Average wood chip density influences chlorite holopulp fiber strength. $R^2 = 0.94$.

low pulp strength.

The chips were then analyzed to determine if there was a change in wood quality typical of a reliance on more plantation wood in winter. The density and average growth increment were measured on the retained 13-mm and retained 19-mm size fractions. The difference in density between the three periods is small and not as large as would be expected with a significant shift in wood source. The growth ring widths are also quite similar at 3 to 4 mm and are only significantly higher in the 13-mm size category. Typical plantation wood has growth rings of 6 mm or larger. Approximately 10% of the growth rings measured in the spring wood samples are in this size range compared to 12% for both winter and summer and 19% for the second winter sample used as a control.

Although none of these differences appeared to be particularly significant, the ranking by percent of large growth rings matched ranking by wood density, and both density and percentage of large growth rings match the relative order of native fiber strength for the four periods. When the wood density is plotted against average zero-span tensile index, a straight line relationship is obtained with an R^2 of 0.94 (Fig. 8). Based on the results of a wood density project carried out at the Georgia Tech Center for High Yield Pulp Science, a 0.03 g/cc increase in wood density can increase TMP burst index by 40 to 50% and tear by about 15%.[13]

Conclusions:

Using the holopulping process to evaluate fiber strength losses in thermomechanical pulping has succeeded in tracing the seasonal strength loss observed by the Bowater TMP mills to a decrease in wood fiber strength during the winter and summer. This fiber weakness shows up as low wood chip and refiner holopulp zero-span tensile index and low holopulp tear index at constant tensile index. Fiber length is also lower in the winter and summer refiner samples. An analysis of the wood chips for the three seasons evaluated shows a slight increase in oversized chips during the winter and summer periods, and a decrease in the wood density of the winter and summer samples. In addition, there is an increase in the number of chips with large growth rings observed in winter and summer. This is an indication of a higher juvenile wood or plantation wood content. The observed change in wood density is sufficient to induce the changes in strength observed in the mill. It needs to be emphasised that the fiber strengths observed in the TMP holopulps greatly exceeds the strength obtained in mill TMP. The mill paper strength is still bond strength limited in these samples, and an appropriate choice of refining conditions may provide the bond strength and paper strength desired.

Acknowledgement:

We would like to express our thanks to Bob Harley of Bowater Corporation, and the Bowater Southern Mill in Calhoun, Tennessee, for providing an interesting problem and the samples to study it. We thank the TMP mill operators and staff for their effort to reproduce the controlled refining conditions on a periodic basis and Melanie Gray and Shawn Wendell who collected all the samples and mill data to support the project. Finally, we thank the members of the Mechanical Pulping Project Advisory Committee for their advice and support of the project and for the member companies of the Institute of Paper Science and Technology who provided the financial support for the project.

EXPERIMENTAL:

Chlorite Holopulping:

A stock buffered chlorite solution is prepared as follows: To a 1-liter volumetric flask, add approximately 500 ml of distilled water, 60 g (0.66 moles) of reagent grade sodium chlorite and 60 g (0.72 moles) of reagent grade sodium acetate. Dilute to the mark with distilled water. Place 50 g (OD basis) wood chips in a 500 ml Erlenmeyer flask. Add 300 ml of buffered sodium chlorite solution and 20 ml of reagent grade glacial acetic acid. Attach the flask to a vacuum source and evacuate the flask to improve penetration of the chlorite solution into the chip. At room temperature the wood chips will take 4 to 5 days to consume the majority of the chlorite. The sodium acetate buffer will maintain a pH around 4. Filter the wood chips and wash once with distilled water. Transfer the chips back into the Erlenmeyer flask and add sufficient distilled water to cover the chips. Let the wood soak in the distilled water overnight and filter again or decant the wash water. Add 200 ml of 0.15 N NaOH, cover the Erlenmeyer flask, and let the wood soak for 24 hours. Filter or decant the alkaline solution and check the pH. If below 9.0, repeat the caustic extraction by adding another 200 ml of 0.15 N NaOH and letting the chips soak another 12 to 24 hours. Filter and wash the chips thoroughly. Place them back into the Erlenmeyer flask and repeat the chlorite procedure as described above with the following exception: use 200 ml of chlorite stock solution and 20 ml of acetic acid. Repeat until the chips are fully delignified. After four delignification cycles, the chips are broken up in the British Disintegrator (3000 revolutions). Once the chips are broken into fibers, the filtrates tend to plug filter paper and a 150 mesh wire screen is substituted for filter paper in the Büchner funnel. A final chlorite treatment is required to complete the pulping process. The pulp is then washed thoroughly and disintegrated another 3000 revolutions.

Fiber length was determine using the Kajaani FS-100 optical fiber length analyzer. Samples were screened on a 0.2-mm Valley slot screen prior to making handheets. Handsheets were prepared (TAPPI T-205) and tested for tensile index, tear index, scattering coefficient, and absorption coefficient according to TAPPI 220. Zero-span tensile index was carried out according to TAPPI T-231.

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13. Wood density study perfomed by Herty Foundation, the Georgia Institute of Technology Center for High Yield Pulp Science and IPST. The results of this project are reported in the IPST 1991 Annual Research Review, Mechanical Pulping Session under Project 3566.

Table 1: Student *t* values for pooled Zero-Span Tensile Index data.

	Winter		Spring		Summer	
	Normal	Control	Normal	Control	Normal	Control
Z-Span $N \cdot m^2/g$	139	139	150	152	142	144
WinNorm	0	-0.218	**3.230**	**3.668**	0.621	1.627
WinCont	-0.218	0	**3.693**	**4.130**	0.912	**2.059**
SprNorm	**3.230**	**3.693**	0	0.526	**-2.706**	**-1.918**
SprCont	**3.668**	**4.130**	0.526	0	**-3.169**	**-2.425**
SumNorm	0.621	0.912	**-2.716**	**-3.169**	0	0.994
SumCont	1.627	**2.059**	**-1.918**	**-2.425**	0.994	0

Entries in bold print are significantly different. $t_{crit.}$ = 2.977 for a 99% confidence level two tailed test, 2.145 for a 95% confidence level two tailed test, and 1.761 for a 95% confidence level one tailed test.

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